A novel inkjet printed surface enhanced Raman spectroscopy (SERS) substrate for the detection of toxic heavy metals

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Abstract

A novel surface enhanced Raman spectroscopy (SERS) substrate was successfully fabricated on a silicon (Si) wafer using a 400 nm inkjet printed thin film of silver (Ag) nanoparticle ink, with 150 nm particle size. The capability of the fabricated SERS substrate for detecting toxic heavy metals such as mercury sulfide (HgS), cadmium sulfide (CdS) and zinc oxide (ZnO) was demonstrated. The SERS based response of the printed substrate produced an enhanced Raman signal when compared to that of target molecules adsorbed on bare Si wafer. An amplification of the SERS intensity by an order of 3 to 5 times was observed for all test samples, due to the presence of hotspots between the metal nanoparticle aggregates. The responses demonstrated the feasibility of the novel SERS substrate to be used in applications for detection of toxic heavy metals.

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1. Introduction

Over the past few decades, there has been an increasing interest in the development of highly sensitive and versatile systems for the detection of trace amounts of toxic heavy metals that are a major cause of environmental pollution [1]. Toxic heavy metals, common pollutants found in water and soil, are known to have hazardous effects on humans, animals and wildlife which can affect the brain, the nervous system and can cause bone diseases [2]. Various techniques such as plasma mass spectrometry [3], colorimetric analysis [4] and UV-vis spectroscopy [5] have been used for the detection of heavy metals. Generally these techniques are time-consuming and laborious as they would require pre-treatment of test samples. Surface enhanced Raman spectroscopy (SERS) has been shown to overcome the drawbacks of these

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traditional techniques with added advantages such as: rapid response, and high sensitivity and selectivity [6, 7]. In addition, the capability to give real-time molecular level vibrational information has demonstrated the potential of SERS to be used as an analytical tool for trace detection of biochemical molecules [8-10].

Enhancement of Raman spectra, from SERS, has been obtained through the roughening of silicon (Si) substrates by using electron beam lithography [11]. A similar roughness can be obtained by immobilizing metallic nanoparticles (NP) on a Si wafer. Inkjet printing of organic and nanoparticle inks have been successfully applied for immobilizing NPs on Si wafers [12, 13]. However, there are no reports on inkjet printing of NPs on Si wafers as a SERS platform.

In this work, we use inkjet printing for fabricating a novel SERS substrate on a Si wafer by employing a thin film of silver (Ag) nanoparticle ink for detecting toxic heavy metals. Ag nanoparticle ink was chosen due to its proven ability to enhance the Raman effect of various test samples [14]. The capability of the printed SERS substrate will be exhibited through the detection of toxic heavy metals such as mercury sulfide (HgS), cadmium sulfide (CdS) and zinc oxide (ZnO).

2. Experiment

CdS, HgS, ZnO (all in crystalline form) and Ag nanoparticle ink with 150 nm particle size (in aqueous form) were purchased from Sigma-Aldrich chemical company. A 4 inch (100) Si wafer was used as the SERS substrate. 25 mM, 45 mM and 75 mM concentrations of CdS, HgS and ZnO were prepared by mixing 25 mg of the heavy metals in 5 ml of deionized (DI) water.

A 400 nm thick film of Ag nanoparticle ink was inkjet printed on the Si wafer, using a DIMATIX inkjet printer (DMP 2831), as an array of 21 squares each having an area of 1 cm by 1 cm. The ink was loaded into a DIMATIX DMC-11610 cartridge (10 pl) through a 25 mm disposable Whatman syringe filter, with a PVDF filter membrane of 0.45 μm pore size, which is used to remove the large particles in order to achieve smooth printing. The printed substrate was then cured in a VWR 1320 temperature controlled oven for 30 min at 100 °C. Figure 1a shows a photograph of the inkjet printed silicon wafer.

The experiment setup is shown in Fig. 1b. The toxic heavy metal analytes were transferred onto the bare Si wafer as well as the Ag nanoparticle printed area of the Si wafer. A laser source in the near infrared region with a wavelength of 785 nm was used to excite the sample using a Raman probe (Inphotonics Inc.), with an integration time of 1 second at 300 mW. A spectrometer (QE 65000 Ocean Optics, 780 nm - 1100 nm) was employed to obtain the Raman spectra through the collection fiber of the Raman probe. The Raman spectra was then analyzed using Spectra Suite software (Ocean Optics) for the Raman signature spectra of the target molecules.

![Fig. 1. (a) Inkjet printed silicon substrate; (b) Experimental setup for SERS.](image-url)
3. Results

Figure 2a shows the SERS based response of the inkjet printed substrate towards HgS. The Raman spectra obtained from the test analytes on the bare Si wafer are overlain with the spectra obtained from the test analytes on the Ag nanoparticle coated Si wafer. Similarly, the spectra for CdS and ZnO are shown in Fig. 2b and Fig. 2c, respectively. Characteristic Raman peaks for HgS, CdS and ZnO were observed at 249.13 cm\(^{-1}\), 299.41 cm\(^{-1}\) and 415.25 cm\(^{-1}\), respectively and for that of Ag nanoparticles were observed at 918.49 cm\(^{-1}\) and 1391.18 cm\(^{-1}\). The SERS based response of the printed sensor revealed an enhanced Raman effect by an amplification factor of 5, 3 and 4 for HgS, CdS and ZnO, respectively immobilized on Ag nanoparticle printed substrate when compared to that of HgS, CdS and ZnO immobilized on bare Si wafer.

Raman Spectroscopy is based on the elastic and inelastic scattering of the photons in the target molecules. Depending upon the nature of the target molecules, each photon undergoes different levels of scattering, thus facilitating the differentiation between each species. The amplification of the Raman effect can be attributed to a change in frequency due to the enhancement of the electromagnetic field at hotspots, which is the area between two neighbouring nano-particles [15]. This enhancement of the electromagnetic field is facilitated because of the embedding of target molecules between adjacent nanoparticles.

![Mercury Sulfide (HgS)](image)

![Cadmium Sulfide (CdS)](image)

![Zinc Oxide (ZnO)](image)

Fig. 2. (a) Comparison of the Raman spectrum of HgS on Ag nanoparticle printed substrate vs. HgS on bare Si wafer; (b) Comparison of the Raman spectrum of CdS on the Ag nanoparticle printed substrate vs. CdS on bare Si wafer; (c) Comparison of the Raman spectrum of ZnO on Ag nanoparticle printed substrate vs. ZnO on bare Si wafer. The spectra were obtained using 785 nm excitation with an integration time of 1 second at 300 mW.
4. Conclusion

We have successfully designed and fabricated a novel SERS substrate by inkjet printing Ag nanoparticle ink on a Si wafer. We have demonstrated the capability of the printed substrate to produce an enhanced Raman effect by testing toxic heavy metals such as (HgS), CdS and ZnO. An amplification factor of 5, 3 and 4 for HgS, CdS and ZnO, respectively immobilized on the Ag nanoparticle printed substrates was observed when compared to that of HgS, CdS and ZnO immobilized on a bare Si wafer. Further studies are in progress to develop the inkjet printed substrate to be used in SERS based hand-held systems for a wide range of biochemical sensing applications. The rapid and easy nature of fabricating this sensor would also help in the production process by significantly reducing the cost per unit.

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References


